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(54) QUARTZ GLASS CRUCIBLE FOR PULLING SILICON SINGLE CRYSTAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a quartz glass crucible which makes it possible to continuously pull a non-transition single crystal for a long time by uniformly producing the crystal phase of quartz glass in a short time on the inside surface of the quartz glass crucible.

SOLUTION: The characteristics of this quartz glass crucible for pulling a silicon single crystal comprises having a arithmetical average roughness of 0.02 to 20 μ m on the surface of a quartz glass base material on the quartz glass crucible inside surface with which at least a melted silicon liquid is brought into contact and further having the coating film of a substance having a higher melting point than the melting point of the silicon in a thickness of 0.01 to 50 μ m on the surface of the base material.

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CLAIMS

[Claim(s)]

[Claim 1]In a silica glass crucible inner surface which will touch silicon melt at least, A silica glass crucible for silicon crystal pulling which a silica glass base material surface is the arithmetic mean roughness which is 0.02 micrometer – 20 micrometers, and has a coated layer of a substance which is a high-melting point by a thickness of 0.01 micrometer – 50 micrometers rather than the melting point of silicon in this base material surface, and is characterized by things.

[Claim 2]In a silica glass crucible inner surface which will touch silicon melt at least, A silica glass crucible for silicon crystal pulling which a silica glass base material surface is the arithmetic mean roughness which is 0.02 micrometer – 20 micrometers, and has a layer which contains a silica particle of 5 – 90 volume % from this inner surface to a surface field less than 1 mm thick, and is characterized by things.

[Claim 3]In a silica glass crucible inner surface which will touch silicon melt at least, A silica glass crucible for silicon crystal pulling which has a coated layer with a thickness of 0.01 micrometer – 50 micrometers which becomes the outermost surface of a silica glass crucible from a substance which is a high-melting point rather than the melting point of silicon, has a 20 micrometers – 5 mm-thick crystalline substance silica layer inside this enveloping layer further, and is characterized by things.

[Claim 4]The silica glass crucible for silicon crystal pulling according to claim 3 which is what said crystalline substance silica layer forms by a phase transformation of silica glass by holding in temperature of 1200–1650 **.

[Claim 5]The silica glass crucible for silicon crystal pulling according to claim 1, 3, or 4 whose crystal grain diameters of said coated layer are 0.005 micrometer – 1 micrometer.

[Claim 6]The silica glass crucible for silicon crystal pulling according to claim 1, 3, or 4 whose presentation of said coated layer is a compound or titanium of titanium, carbon, and/or nitrogen.

[Claim 7]The silica glass crucible for silicon crystal pulling according to claim 1, 3, or 4 whose presentation of said coated layer is a presentation which contains an oxide of an element more than a kind at least among titanium, calcium, barium, and aluminum.

[Claim 8]A silica glass crucible for silicon crystal pulling characterized by a field (20 micrometers – 5 mm) being a crystalline substance silica layer from this silica glass crucible inner surface in a silica glass crucible inner surface which will touch silicon melt at least.

[Claim 9]After said crystalline substance silica layer forms a layer containing a silica particle of 5 – 90 volume % in a surface field less than 1 mm thick from a silica glass crucible inner surface, The silica glass crucible for silicon crystal pulling according to claim 8 which is what is formed by a phase transformation of silica glass by holding in temperature of 1200–1650 **.

[Claim 10]The silica glass crucible for silicon crystal pulling according to claim 9 in which said silica particle is a crystalline substance silica particle.

[Claim 11] The silica glass crucible for silicon crystal pulling according to claim 9 in which said silica particles are cristobalite particles.

[Claim 12] A silica glass crucible for silicon crystal pulling given in any 1 paragraph of claims 3-11 which are the arithmetic mean roughness whose base material surfaces of said silica glass crucible are 0.02 micrometer - 20 micrometers.

[Claim 13] The silica glass crucible for silicon crystal pulling according to claim 1, 2, or 12 which is maximum roughness (Rmax) and the minimum granularity (Rmin) with which surface roughness of said silica glass base material is further satisfied of the following expression of relations. $R_{max}/R_{min} \leq 10$

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the silica glass crucible used for the silicon crystal pulling by the Czochralski method (a CZ process is called below).

[0002]

[Description of the Prior Art] Conventionally, the crystal pulling method called what is called a CZ process is widely adopted as manufacture of a silicon single crystal industrially. This method carries out heat melting of the polycrystalline silicon within a container, and it is pulled up, soaking the end of the seed crystal of silicon in this melting bath, and making it rotate, and the single crystal which has the same crystal orientation on a seed crystal grows. The silica glass crucible is generally used for the raising container of this single crystal. Here, silica glass is a name of silica (SiO_2) glass. The silica glass crucible which put in polycrystalline silicon is heated for a long time more than the melting point (about 1414 **) of silicon, and since it is put to silicon melt, the inner surface gestalt of a silica glass crucible changes gradually. As a result, when a silica glass crucible is used for a long time, an erosion (a glass surface should corrode) and devitrification (whiten, when transparent glass crystallizes) will arise, and it will have the serious influence for manufacture of a silicon single crystal. If the impurity is especially contained in the silica glass crucible so much, this impurity also dissolves, it will become a cause of the impurity contamination to a silicon single crystal, or it will cause [it will be incorporated into silicon melt, and an impurity will promote crystallization of silica glass, and] the characteristic degradation of the silica glass crucible by devitrification. For this reason, the silica glass crucible is manufactured considering the quartz powder of a high grade as a raw material. Although living rock English powder is mainly used as this charge powder for crucibles of Ishihara now, the synthetic quartz powder whose purity is higher than living rock English powder is also used, and careful attention is paid to mixing of the impurity.

[0003] By the way, this silica glass crucible has the function to transmit the heat from the carbon heater currently installed in the outside of a crucible to melt while holding silicon melt. Large caliber-ization of the silicon wafer in recent years has brought about enlargement of a silica glass crucible, and the increase in the amount of silicon to dissolve, and, as a result, the heat load from a heater is large by the silica glass crucible wall part. In order to hold a lot of silicon melt and to perform silicon crystal pulling, the contact time of

silicon melt and a silica glass crucible inner surface is long. For this reason, even if it is the silica glass crucible which controlled impurity mixing, the amount of erosions from a crucible inner surface to melt increases, crystallization of the silica glass on the surface of a crucible advances gradually, and the crystal phase (cristobalite) of punctate silica glass becomes is easy to be formed in a crucible inner surface. The generation place of the crystal phase of silica glass is not necessarily constant, and it concentrates on a specified part, or many cases of being uneven are seen. In other words, it will be in the state where it crystallized selectively. The glass phase of the dissolution rate to the silicon melt of silica glass is quicker than a crystal phase, the uneven dissolution follows the silica glass crucible inner surface which contacted silicon melt for a long time, and surface roughness becomes large. On the other hand, inside the glass of a silica glass crucible, when a large number [air bubbles], these are released in silicon melt because the erosion of silica glass progresses, and surface roughness may become large. Thus, the portion to which surface unevenness became large tends to secede from a crucible inner surface, and the section from which it seceded floats the inside of silicon melt. It adheres to the silicon single crystal growth interface which this is raising, and serious quality defects, such as polycrystal-izing or formation of an owner rearrangement, are caused. This is a life by functional degradation which is called owner rearrangement-ized generating unlike a structural life like the shape distortion by an elevated temperature. For this reason, prolonged use of the silica glass crucible became difficult, and had caused the rise of silicon single crystal production cost.

[0004]In order to solve the problem of partial crystallization of such silica glass, OH concentration and alkaline metal concentration in silica glass are lowered and high-grade-ized, The method of controlling crystallization is proposed by JP,3-208880,A, JP,8-133719,A, JP,5-301731,A, etc. Although crystallization is controlled to be sure, since it was difficult to reduce all the impurity contents in a silica glass crucible to a limit actually according to these methods, crystallization arose selectively and the roughness of the silica glass inner surface by uneven crystallization and dissolution was not avoided.

[0005]On the other hand, reversely, there is an idea of crystallizing silica glass positively. Silica glass metamorphoses into various crystal phases, such as cristobalite, Quartz, and a TORIDE dynamite. For example, if silica glass is made into the elevated temperature more than near a glass transition point (about 1200 **) in ordinary pressure (or low pressure), it will crystallize gradually to beta-cristobalite (the melting point is about 1710 ** at the parent phase of cristobalite). Although crystal growth speed serves as the maximum at about 1650 **, it is known that it is so high that it is sensitive also to atmosphere and an oxygen density and water vapor pressure are high. As a method of promoting this crystallization, the following three techniques are mainly indicated until now.

[0006]The method of crystallizing the 1st is distributing the crystallization accelerator in silica glass crucible construction material. The method of using an aluminum oxide etc. as a crystallization auxiliary agent, and carrying out mixture dispersion to material quartz powder at the time of silica glass manufacture, is indicated in the JP,5-24870,A gazette. However, even if the impurity which promotes crystal growth existed, the nucleation probability from the inside of the quality of a glass material required still more nearly excessive time, before crystal nucleation took the long time and the whole crucible crystallized, since it was very lower than the nucleation probability in the surface. Since it was finely divided when metamorphosing into alpha-cristobalite from beta-cristobalite near 270 ** (beta-alpha transformation) when room

temperature cooling was carried out after the whole crucible crystallized at the elevated temperature, cleaning took time and effort. Since room temperature cooling accompanied by a beta-alpha transformation was accompanied by glass breakage when the whole crucible was once crystallized, there were restrictions of making it crystallize within a crystal-pulling furnace.

[0007]By the method of crystallizing the 2nd making a crystallization accelerator alkali metal ion, alkaline earth metal ion, etc., and forming the sandwich structure which sandwiches the layer containing a crystallization accelerator by the quartz glass layer of two sheets, Crystallizing the quartz glass layer of a crucible inner surface from an internal crystallization promoting layer, when heating is indicated by JP,11-199370,A. However, the restrictions of making it crystallize within a crystal-pulling furnace were, and also even if the crystallization accelerator existed in the inside, since the nucleation probability from the inside of the quality of a glass material was low, there was a problem that crystallization of glass took a long time.

[0008]The method of crystallizing the 3rd applies a crystallization accelerator to the silica glass crucible surface. 2a group elements, such as magnesium, strontium, calcium, and barium, etc. are applied to a silica glass crucible inner surface, and the method which make a crystal layer easy to form at the time of the dissolution of a silicon raw material is proposed by JP,8-2932,A and JP,9-110590,A. However, the point that a coating film exfoliates easily in coating liquid like alcoholic water content when the adhesion force to a quartz glass surface sets the lump of the silicon polycrystal which should dissolve weakly, There were faults, such as a point which is not so high, therefore a point that the uniform crystallization effect is not acquired at an early stage.

[0009]Although the above measures have been taken until now, in a severe operating environment which was described previously, the further, chemically stable silica glass crucible is called for. For that purpose, it needs further to be improved for making the target thickness generate a crystal phase uniformly for a short time by controlling intrinsically generation and growth of the crystal phase of the silica glass in a silica glass crucible inner surface.

[0010]

[Problem(s) to be Solved by the Invention]This invention solves the above-mentioned problem in the conventional silica glass crucible, and makes the crystal phase of silica glass generate uniformly by a silica glass crucible inner surface for a short time, and an object of this invention is to provide the silica glass crucible which is equal to prolonged use.

[0011]

[Means for Solving the Problem]As a result of this invention persons' repeating a research experiment and adding examination wholeheartedly, the crystallization effect increases synergistically by combining two or more effective crystallization techniques, Make one time generate a crystal phase of silica glass uniformly all over a quartz glass surface by raising nucleation density of a crystal phase of silica glass remarkably, and. Without a crystal layer all **(ing), even if it contacted silicon melt for a long time, when only the target thickness grew up a crystal phase also into a thickness direction of silica glass uniformly, wafer exfoliation from a silica glass crucible inner surface was lessened, and it found out that a life of a crucible was extensible. If crystal layer thickness is controlled to 1 mm or less even if it crystallizes a silica glass crucible inner surface as a result of repeating various examinations, It checks not dividing or exfoliating, even if it

cools to a room temperature, and finds out that crystallization of glass can be crystallized also in a general-purpose and comparatively cheap general-purpose heating furnace which can choose freely preset temperature only in [expensive] a raising furnace, and atmosphere, and this invention is completed.

[0012]That is, this invention is (1). In a silica glass crucible inner surface which will touch silicon melt at least, A silica glass base material surface is the arithmetic mean roughness which is 0.02 micrometer – 20 micrometers, And a silica glass crucible for silicon crystal pulling which has a coated layer of a substance which is a high-melting point by a thickness of 0.01 micrometer – 50 micrometers rather than the melting point of silicon in this base material surface, and is characterized by things, (2) In a silica glass crucible inner surface which will touch silicon melt at least, A silica glass base material surface is the arithmetic mean roughness which is 0.02 micrometer – 20 micrometers, And a silica glass crucible for silicon crystal pulling which has a layer which contains a silica particle of 5 – 90 volume % from this inner surface to a surface field less than 1 mm thick, and is characterized by things, (3) In a silica glass crucible inner surface which will touch silicon melt at least, It has a coated layer with a thickness of 0.01 micrometer – 50 micrometers which becomes the outermost surface of a silica glass crucible from a substance which is a high-melting point rather than the melting point of silicon, A silica glass crucible for silicon crystal pulling and (4) which furthermore have a 20 micrometers – 5 mm-thick crystalline substance silica layer inside this enveloping layer, and are characterized by things Said crystalline substance silica layer, A silica glass crucible for silicon crystal pulling given in (3) which is what is formed by a phase transformation of silica glass by holding in temperature of 1200–1650 **, (5) (1) whose crystal grain diameters of said coated layer are 0.005 micrometer – 1 micrometer, (3) Or a silica glass crucible for silicon crystal pulling given in (4), (6) (1) whose presentation of said coated layer is a compound or titanium of titanium, carbon, and/or nitrogen, (3) Or a silica glass crucible for silicon crystal pulling given in (4), (7) (1) whose presentation of said coated layer is a presentation which contains an oxide of an element more than a kind at least among titanium, calcium, barium, and aluminum, (3) Or a silica glass crucible for silicon crystal pulling given in (4) and (8) In a silica glass crucible inner surface which will touch silicon melt at least, A silica glass crucible for silicon crystal pulling characterized by a field (20 micrometers – 5 mm) being a crystalline substance silica layer from this silica glass crucible inner surface, (9) After said crystalline substance silica layer forms a layer containing a silica particle of 5 – 90 volume % in a surface field less than 1 mm thick from a silica glass crucible inner surface, A silica glass crucible for silicon crystal pulling given in (8) which is what is formed by a phase transformation of silica glass by holding in temperature of 1200–1650 **, (10) A silica glass crucible for silicon crystal pulling given in (9) said whose silica particle is a crystalline substance silica particle, (11) A silica glass crucible for silicon crystal pulling given in (9) said whose silica particles are cristobalite particles, (12) A silica glass crucible for silicon crystal pulling of any one statement of (3) – (11) which is the arithmetic mean roughness whose base material surfaces of said silica glass crucible are 0.02 micrometer – 20 micrometers, (13) Surface roughness of said silica glass base material is a silica glass crucible for silicon crystal pulling given in (1) which is maximum roughness (R_{max}) and the minimum granularity (R_{min}) which satisfy the following expression of relations further, (2), or (12), and R_{max}/R_{min}<=10.

[0013]

[Embodiment of the Invention]This invention is explained in detail below.

[0014]In order to pull up a silicon single crystal for a long time, it is important to control the formed state of

the crystal phase of the silica glass formed in a crucible inner surface. Originally silica glass is not stable as a glass phase, and a cristobalite phase or its TORIDI dynamite phase is thermodynamically stable in the temperature range from which a silicon single crystal is pulled up. Therefore, even if it makes the impurity in silica glass there be nothing, crystallization of a quartz glass surface is not avoided in essence.

Crystallization of silica glass takes place easily by an interface with melt with large surface energy and substance diffusion more frequent than the inside of glass.

[0015]The crystal phase of silica glass is formed in punctate in a quartz glass surface, and the formation can be divided into a nucleation and crystal growth, and can be considered. That is, the number of the spot of a quartz glass surface is equivalent to the amount of karyogenesis, and change of the size of a spot is equivalent to a growth rate. And in the quartz glass surface immersed in melt, the core of the crystal phase of silica glass generated immediately after immersion from the experiment in which the silica glass of various surface states is made immersed to silicon melt, and it became clear to grow up in proportion to immersion time after that. And the spot of the crystal phase of the silica glass formed in the quartz glass surface showed the size according to immersion time, and it became clear in the silica glass of the same presentation that the rate of crystal growth was constant. When crystal phases contacted with growth of the crystal phase of silica glass, the crystal growth of the plane direction ceased by the crystal phase interface which contacted, and ***** of the crystal phase did not happen, but it also became clear that crystal growth progresses to a depth direction chiefly. It is shown that disappearance of the crystal phase in which this is new after a nucleation happens to one time in a quartz glass surface and which was nucleated and generated is a mechanism which it does not happen but the total amount of the crystal phase of silica glass increases only with crystal growth. And the nucleation of the crystal phase of silica glass is greatly influenced according to the surface state of silica glass. Then, by this invention's carrying out densification of the starting point of this nucleation intentionally, and crystallizing the silica glass of a crucible inner surface uniformly extremely for a short time, and carrying out growth promotion of the crystallization of silica glass to the thickness direction of a crucible chiefly, It is considered as the silica glass crucible which is equal to prolonged use in silicon crystal pulling. the surface roughening of a crucible inner surface which is described below by this invention -- and, The art of formation of the crystalline layer by the thermal pretreatment after giving the crystallization technique of grant and such a crystallization technique to a crucible internal surface of crystallization promoting agent called the coat formation of a crystalline substance or seeding of a silica particle which consists of a different presentation from silica glass is combined complexly.

[0016]The fundamental invention of the 1st of this invention carries out surface roughening of the inner surface of a silica glass crucible uniformly, and it is a silica glass crucible which covers the inside with a different crystalline layer from a silica glass presentation. Usually, the nucleation of the crystal phase of silica glass happens easily by the part where change of the surface energy in a quartz glass surface or surface energy is large. Specifically, they are the portion to which impurity particles stuck, a portion with a structure defect, etc. In order to build change of this surface energy intentionally, it is simple on the surface to give uniform and detailed unevenness, it is effective for it, and the nucleation part of the crystal phase of silica glass can be formed uniform very with high density by covering with the crystalline layer which serves as a core of a crystal phase further. And in order that the crystal phase of silica glass may cover all crucible

inner surfaces extremely for a short time. Growth of the crystal phase of silica glass serves as a thickness direction of a crucible chiefly, and the crystal phase formed in a silica glass crucible inner surface is made thickly uniformly. Even if it uses it for a long time, there is no surface roughness by the difference in the dissolution rate of the silica glass crucible surface to silicon, and exfoliation of a silica section serves as few silica glass crucibles for silicon crystal pulling.

[0017]Now, the surface roughening of the above-mentioned crucible inner surface, therefore unevenness of a rough surface must be the surface roughness which is 0.02–20.0 micrometers of arithmetic mean roughness.

[0018]Arithmetic mean roughness is displayed as Ra and known as a parameter showing the surface roughness of various industrial commodities. About the definition and display, JIS B-0601 has a statement in detail. In the international standard, ISO 468, ISO 3274, ISO 4287, and ISO4288 grade are supported. Only reference length is sampled in the direction of that mean line from a roughness curve, the X-axis is taken in the direction of the mean line of this sampling portion, it takes a Y-axis in the direction of longitudinal magnification, and Ra expresses with the micrometer (micrometer) the value which integrated with the roughness curve to the center line. The contact process which measurement of surface roughness is contacted to a specimen surface using the needle of the non-contact method by light, laser, etc. and stable materials, such as a diamond, and is measured is known.

[0019]The arithmetic mean roughness (Ra) of the inner surface of the conventional silica glass crucible is the about 0.002–0.01-micrometer smooth surface. This is supplied in the mold turning around silica powder, and forms a silica powder packed bed, by the arc heating which carried out the control atmosphere of it, melting and in order to make it dissolve and to form a crucible inner surface, it becomes smooth unescapable, and control of surface roughness cannot be performed only by this method. The field which gave unevenness to the surface intentionally will be called a split face. The arithmetic mean roughness of a split face causes an erosion with an uneven crucible inner surface, in order that the homogeneity of a nucleation may be spoiled and all may form a crystal phase in a quartz glass surface unevenly, if larger [when smaller than 0.02 micrometer, there are few nucleation facilitatory effects, and] than 20 micrometers.

[0020]The granularity of a split face requires that values should not differ greatly within the same crucible. Since the nucleation density of the crystal phase of silica glass is influenced with surface unevenness, this is important because of crystal phase formation of the uniform silica glass within the same crucible. For this reason, as for the ratio (Rmax/Rmin) of the maximum to the minimum of the granularity of a split face, it is desirable that it is ten or less. Since the crystal phase formed in the portion of big granularity will become easy to break away if this ratio exceeds 10, it is not desirable.

[0021]Although a split face may be given only within the part which the homogeneity in a crucible wants to crystallize, the part which touches silicon melt at least is made into a split face. Since especially the pars-basilaris-ossis-occipitalis inner surface of a crucible certainly contacts silicon melt and contact time also becomes longer than the inner surface in other crucibles, a pars-basilaris-ossis-occipitalis inner surface needs to consider it as a split face. The place which does not contact silicon melt in the portion near the opening of a silica glass crucible does not need to be uneven on the surface, and if a conversion cost and time and effort are taken too much, it is not necessary to make it into a split face.

[0022] Such a silica glass crucible for silicon crystal pulling contacts the particles or material whose surface hardness is higher than silica glass with fixed stress to this silica glass crucible inner surface, and can be manufactured by giving unevenness to a crucible inner surface. Under the present circumstances, the split face whose Ra of a crucible is 0.02–20 micrometers is acquired by using the hard grain whose particle diameter is 0.01–40 micrometers. Or arithmetic mean roughness may use the hard material which is 0.01–40 micrometers. Formation of a split face needs to carry out with fixed stress, and, for the purpose, its belt sander and grinding stone using an electrical motor are more preferred than the method of making the surface coarse by hand using sandpaper, for example so that dispersion in the arithmetic mean roughness within a single crucible may be set to $R_{max}/R_{min} \leq 10$. Formation of a split face may be performed in a drying atmosphere, and it does not matter even if it carries out in a solution. In the solution which carries out a chemical reaction to silica glass, the above-mentioned hard grain and hard material may be made to contact, and unevenness may be given to the surface using chemical machinery scouring.

[0023] As a material whose surface hardness is higher than silica glass, the carbide of silicon or titanium, a nitride, carbon nitride, alumina, a diamond, boron nitride, high grade quartz, etc. can use it industrially. These may be in the state covered also with a simple substance or particle state. For example the method of attaching unevenness mechanically installs a grinding machine in a silica glass crucible, rotates a crucible, and can be manufactured using the grinding tool which consists of material whose surface hardness is higher than the above-mentioned silica glass. Or the method of spraying the above-mentioned hard grain on a silica glass crucible inner surface with high-pressure gas, and attaching unevenness to the surface is also possible. It is also possible to distribute the above-mentioned hard grain in a solution, to make particles collide with a silica glass crucible inner surface using an ultrasonic washing machine, and to give unevenness.

[0024] By the method of making the surface of these crucible inner surfaces coarse, when the above-mentioned hard material or its part adheres to a silica glass crucible inner surface, it is necessary to consider so that an affix may not have an adverse effect on silicon single crystal raising. For example, when it seems that silicon carbide has adhered, it dissolves into silicon melt, the carbon concentration in a silicon single crystal is raised during raising, and quality is degraded, it can avoid by lessening coating weight or washing. It is solvable also by the process of using other hard material, and the device of the material of construction. On the contrary, there is no influence of the quality on a silicon single crystal, and when the nucleation of cristobalite and growth are promoted by the affix, an affix may be used positively. When attaching unevenness to the surface using a chemical operation, it is effective if the solution which carries out a chemical reaction to silica glass, and is dissolved or corroded is used. As such a solution, the solution having contained fluoric acid is suitable. The concentration and temperature of fluoric acid are decided according to surface roughness or processing time. Said quality of a hard object may be included in this solution, and a mechanical work may be used together and surface unevenness may be given.

[0025] Next, the coat of the crystalline substance which consists of a different presentation from the silica glass formed in the outermost surface of the crucible which carried out surface roughening is described. It becomes having made it better [to form a coat in a surface roughening crucible / the adhesion to the quartz glass surface of a coat], and the density of a crystal nucleation place can be increased simultaneously. a crystal nucleation place -- uniform -- density -- in order to make it distributed highly, it is effective to give a precise coat with a small crystal grain diameter. Because of high-density

product-nucleus distribution, it is desirable for the crystal grain diameter of a coat to be 1 micrometer or less. As for a crystal grain diameter, since an effect will fade if a crystal grain is smaller than 0.005 micrometer, it is desirable that it is 0.005–1 micrometer. In order to maintain a fine crystal grain even if it contacts silicon melt when a crystallization facilitatory effect will be lost, if a film substance dissolves, it is required for the melting point of a film substance to be higher than silicon at least.

[0026]The thickness of a coat demonstrates effect sufficient at 0.01 micrometer – 50 micrometers. Since an effect is saturated when thickness was thinner than 0.01 micrometer, the effect used as the product nucleus of a silica glass crystal phase is no longer seen and 50 micrometers is exceeded, and the internal stress of that the formation cost of a coat increases and a coat increases and it becomes difficult to secure adhesion, a thickness of 50 micrometers or less is desirable. Since a coat may react to silicon melt, the dissolution or the erosion of a coat may happen, a dissolution component changes the presentation of silicon melt and the silicon single crystal characteristics which can be pulled up are affected, the thick film over 50 micrometers is not preferred.

[0027]As such a coat, since the compound and/or titanium of titanium, carbon, and/or nitrogen are excellent also in adhesion with silica glass and the endurance in an elevated temperature also has them, specifically, the presentation of a coat is preferred. [expensive] When purity is furthermore needed, the coat whose content of elements other than titanium in a coat, carbon, and nitrogen is 1 or less % of the weight is desirable. Even if it is a coat which consists of a single presentation, it may be the layer film which carried out the plural laminates of these coats. It is easy to crystallize with a fine grain, and these have the far high melting point and it is more preferred than the melting point (about 1414 **) of not less than 2000 ** and silicon. These crystal coating can take the composition ratio of titanium, carbon, and nitrogen broadly. For example, in titanium nitride, in a chemical formula, crystal phases, such as TiN , Ti_2N , and Ti_3N_4 , exist and it can grow also into these composite phases according to a film formation condition. TiN also serves as a crystal phase by presentation wide range from nitrogen 28at% to 60at%. Near 700–800 **, the compound of titanium, carbon, and nitrogen may react to oxygen, and may change to the oxides (for example, TiO_2 , Ti_2O_3 , etc.) of titanium. Even if it becomes an oxide, the effect used as the product nucleus of the crystal phase of silica glass is fully accepted.

[0028]Such a silica glass crucible for silicon single crystal raising can manufacture 0.01–50-micrometer crystal coating by forming in a crucible inner surface by the PVD (Physical Vapor Deposition) method etc. PVD has little load by the temperature to substrates, such as heat modification, it is precise, it has the feature which the crystal coating which consists of fine grains can form, and is suitable for the thin film forming of the crucible inner surface. Specifically as this PVD, the various techniques of vacuum deposition, sputtering, and ion plating can use. All can cover the temperature of a substrate below 500 **, and do not give modification by heat to a silica glass crucible. As for silica glass, it is known that a coefficient of viscosity will become small at a not less than 1000 ** elevated temperature, and the silica glass especially with large weight changes with prudence at an elevated temperature. For this reason, it is necessary to perform a surface treatment at low temperature as much as possible. The three above-mentioned technique has a membrane formation speed as practical as 5 to 50 minutes, although a 1-micrometer coat is obtained at about per minute 0.02–0.2 micrometer, for example.

[0029]Vacuum deposition is the method of dissolving titanium using heat sources, such as an electron beam,

generating the steam of titanium, and vapor-depositing this to a substrate under a vacuum. An equipment configuration is comparatively easy and coat formation cost is the cheapest among the three above-mentioned technique. Sputtering is the method of forming the ingredient which irradiated the target with gas constituents, such as ionized argon, and was begun to beat from this target to a substrate. Since the coat near the presentation of a target is obtained, it is advantageous to formation of a composite film. Ion plating is the method of making the ingredient ionized with plasma react on a substrate, and forming membranes, ion is called by applying an electric charge to a substrate, and high adhesion is acquired, even if it is advantageous to precise coat formation and substrate temperature is low. The coat formation which consists of a crystal of a fine grain in the ion plating method is easy, For example, the arc discharge activation ion plating method which is a kind of the ion plating method is used, and a crystal grain turns into about 0.01-micrometer fine grain in the coat of titanium nitride with a thickness of 1 micrometer which formed membranes by the nitrogen pressure power of 0.05 Pa with the temperature of 300 ** of the substrate. Thus, the forming-membranes method can be chosen according to the characteristic of the target coat.

[0030]The portion covered with PVD does not necessarily need to be the whole silica glass crucible inside surface. In particular, there is a portion which does not contact silicon melt and it is not necessary to cover near the opening of a crucible to this portion. It may be better for thermal efficiency not to give the above-mentioned coat to the portion which does not contact silicon melt, in order to dissolve a silicon raw material efficiently within a crucible. It is more desirable not to cover near an opening with it, when the thermal radiation from the heater on the outside of a crucible is barred by covering. Such a silica glass crucible can be easily manufactured, if the mask of the portion not to cover is carried out with a stainless plate, an aluminum wheel, etc. and the above-mentioned PVD covering is given.

[0031]The coat of the presentation which contains the oxide of the element more than a kind at least among titanium, calcium, barium, and aluminum may be sufficient as another coat. That is, although it is a little inferior to the coat mentioned above also to the oxides and these multiple oxides of titanium, calcium, barium, and aluminum, the growth promotion of the crystal phase of the silica glass from a silica glass crucible inner surface to a thickness direction has an effect. The coat containing these oxides can be formed by applying the suspension of these oxide particles and metal alkoxides to a silica glass crucible inner surface, and drying. Since the direction which should just be 50 micrometers or less and are finer particles as particle diameter of an oxide particle can increase a crystal product nucleus, it is desirable. Since it becomes easy to drop out of a coat and may have an adverse effect on silicon crystal pulling in the particle diameter of more than 50 micrometers, it is not desirable. Although the metal alkoxide can perform coat formation and what is necessary is just not to carry out limitation in particular, since a tetraethoxysilane etc. can obtain easily and it is easy to deal with them, for example, it is suitable. The mixing ratio of an oxide particle and a metal alkoxide is weight ratio conversion, and it is desirable that they are 0.01 to 100 times as many oxide particles to a metal alkoxide. They are 0.1 to 50 times more preferably. At less than 0.01 time, the crystallization facilitatory effect of the silica glass of an oxide particle is not acquired, but coat formation becomes difficult by more than 100 times at a crucible inner surface.

[0032]Next, the fundamental invention of the 2nd of this invention carries out surface roughening of the inner surface of a silica glass crucible uniformly, and it is a silica glass crucible which carries out seeding of

the silica particle to the surface field of this inner surface.

[0033]It is as having mentioned above in the 1st invention about the surface roughening of the inner surface of a silica glass crucible.

[0034]The technique of carrying out seeding of the silica which is crystallization promoting agent with an another coat of the crystalline substance which consists of a presentation different here from the silica glass in the 1st invention is explained. Since the silica particle as crystallization promoting agent is not an impurity like a metallic element, there is an advantage of not becoming a pollution source to silicon wafer manufacture of a high grade. Although it can usually give a surface roughening crucible or a crucible, as for seeding of a silica particle, the adhesion to the quartz glass surface of particles becomes better [way] having carried out seeding to the surface roughening crucible, and simultaneously, it will increase the density of a crystal nucleation place and can bring crystallization of glass forward as a result. carrying out seeding of the core of a silica particle or a crystalline substance silica particle to a silica glass crucible inner surface -- the nucleation part of the crystal phase of silica glass -- intentional -- uniform -- moreover -- density -- by making highly. Even if the crystal phase of silica glass covers all the crucible surfaces and uses it for a long time for a short time, there is no surface roughness by the difference in the dissolution rate of the silica glass crucible surface to silicon melt, and it becomes possible to lessen exfoliation of a section.

[0035]The crystalline substance particles of the above-mentioned silica are distributed over a surface field less than 1 mm thick from the inner surface of a crucible, and volume of the crystalline substance particles of the silica in this range is made 5 to 90%. If larger [when less than 5%, since there is little density of a product nucleus, an effect is thin, and] than 90%, the crystalline substance particles of what not changing will become easy to be desorbed from an effect. Since it is about 5 mm as the thickness of the crystal phase of the silica generated to the inner surface of the quartz crucible for silicon single crystal raising is large, a surface field less than 1 mm thick is used from an inner surface in order for what is necessary to be just to pay its attention to the initial nucleation from the surface in this range. That is, it is because crystallization goes also to the field deeper than it and crystallization of the inner surface of a quartz crucible can fully be promoted, if a surface field less than 1 mm thick is crystallized from an inner surface.

[0036]Burying by an amorphous phase is preferred between the crystalline substance particles of silica. A quartz watch, a TORIDI dynamite, cristobalite, etc. are known and the crystal phase of silica differs in a coefficient of thermal expansion, respectively. These crystal phases metamorphose with heating and are accompanied by a volume change. A quartz watch metamorphoses at 570 **, TORIDI dynamites are 160 ** and 106 **, and displaced-type-transposing is known. To a low temperature form quartz watch being specific gravity 2.65, a high temperature form is specific gravity 2.49, and is accompanied by a volume change when metamorphosing. Although cristobalite also has a high temperature form and a low temperature form and 200 ** – 300 ** have the temperature of transformation, if this temperature is passed at the time of heating or cooling, by about 3.7% of volume change, a crack may arise into a crystal and the surface may exfoliate. Since the amorphous phase between the crystalline substance particles of silica has an effect which absorbs and buffers the volume change of crystalline substance particles, it can make the minimum the property variation of the crucible inner surface by heat. The crystalline substance particles of silica need not to be desorbed from the surface during crucible use. When the crystalline

substance particles of silica are maintained by the crucible inner surface and silicon melt is contacted to the temperature which dissolves silicon from ordinary temperature, it is important that crystal growth is promoted by the core in the crystalline substance particles of silica.

[0037]When silica glass crystallizes, in almost all cases, the crystal phase to generate is a cristobalite phase. Therefore, as for a crystal nucleus, it is preferred that it is cristobalite from the start. What has the content of oxygen close to the stoichiometric composition of 50 to 54 % of the weight and SiO₂ among the crystal phases of silica is preferred. The surface becomes smooth easily and this realizes the uniform dissolution to silicon melt, when a crystal grain is not less than several micrometers, assumes white and touches silicon melt. On the other hand, it turned out that what has oxygen less than the stoichiometric composition of SiO₂ assumes blackish brown by microcrystal grains of 1 micrometer or less, and it breaks away or is easy to dissolve an oxygen content into silicon melt like less than 50 % of the weight. Therefore, as for the crystalline substance particles of silica, it is preferred that it is the cristobalite which 50 to 54 % of the weight of oxygen contains. Also in order to make a core generate uniformly [since the crystalline substance particles of silica are the things used as a crystal nucleus / also in order to raise the density of a core], If it is desirable it to be more effective to be a fine grain as much as possible, and for the maximum droplet size of the crystalline substance particles of silica to be 0.5 mm or less and it is coarse grain from this, it will be hard to demonstrate the operation which raises nuclear density, and the operation which makes a nucleation uniform.

[0038]Such a quartz crucible for silicon crystal pulling, Mixed liquor with the liquid containing the crystalline substance particles and metal alkoxide of silica is applied to the inner surface of a silica glass crucible which touches silicon melt at least, and it calcinates after drying this, and can manufacture by making the crystalline substance particles of silica adhere with sufficient adhesion to a silica glass crucible inner surface. Or the inner surface of a silica glass crucible which touches silicon melt at least is heated at 800–1700 **, where it did not carry out melting of the internal surface and it is softened, the crystalline substance particles of silica are forced, and it can manufacture by embedding the crystalline substance particles of silica to a silica glass crucible inner surface, and making them adhere.

[0039]Although the method of compounding silica glass using a metal alkoxide is called a sol gel process, in this invention, the feature is that it mixes the crystalline substance particles of silica at the time of adjustment of sol. The crystalline substance particles generated from glass by heat treatment of about 1000 ** are cristobalites. Cristobalite particles grind high purity quartz glass to 0.5 mm or less with a mortar etc., for example, and can manufacture it by grinding to 0.5 mm or less with a mortar etc. again after 1300 ** 10-hour calcination with an electric furnace in the atmosphere or under argon atmosphere. At this time, a quartz glass raw material takes care so that there may be no mixing of an impurity, when using the high high grade thing of SiO₂ content as a raw material and grinding it from 99.9%. The sol in the state where the very detailed colloidal particle was first suspended in the fluid is made from a sol gel process, the crystalline substance particles of silica are mixed to this, and it applies to the inner surface of a silica glass crucible. Fixed thickness is obtained that it is easy to apply about 2cp–20cp, and the viscosity of sol is suitable. It is appropriate for the mixed amount of the crystalline substance particles of silica to mix so that it may become 10 to 50% of the weight in sol. After drying this about 10 minutes at a room temperature, making a colloidal particle condense and considering it as the fluid gel which disappeared, By heating at 100 ** –

about 150 ** for 10 to 60 minutes, a solvent is evaporated and a coat with a thickness of 0.01–1 mm containing the crystalline substance particles of the silica combined with amorphous silica glass is made by heating for 60 minutes – 120 minutes, and sintering at an elevated temperature (500 more ** – 700 **). When using a metal alkoxide as a raw material, the silicon alkoxide or silicon methoxide of a high grade is more preferred than 99.99 % of the weight, and it is good to carry out viscosity control with alcohol or water so that it may be easy to apply. When the effect that the one where the particles of the cristobalite used as a crystal nucleus are finer also crystallizes a little addition becomes large and contacts the silicon melt at the time of crucible use, a silica glass crucible inner surface is completely crystallized more in a low-temperature short time. The adhesion of the grain child who is an about 1300 ** elevated temperature and calcinates under the inert atmosphere of argon etc. before use also goes up, and the crucible manufactured by this method is preferred.

[0040]The method of carrying out seeding of another silica is in the state softened without heating the inner surface of a silica glass crucible which touches silicon melt at least at 800–1700 **, and carrying out melting of this crucible inner surface, It is the method of forcing the crystalline substance particles of silica on a crucible inner surface, and making it embed and adhere to this crucible inner surface. This uses the softening phenomenon in the elevated temperature of silica glass. By a high grade thing, although it is about 1700 **, it is not necessary to necessarily heat the melting point of silica glass to directly under [melting point]. It has at least about 800 ** of viscosity. When making it adhere, in order to demonstrate the nucleation effect of the crystalline substance particles of silica to the maximum extent, it is necessary to avoid, and it is 1700 ** or less in temperature, and performs as promptly as possible that the crystalline substance particles of silica recrystallize or dissolve. The crystalline substance silica particle made to adhere has [a thing of 0.5 mm or less] a preferred maximum droplet size, crystalline substance silica particles do not lap but the quantity made to adhere has a preferred 5 to 90% wrap grade in a crucible inner surface. The grade where a crystalline substance silica particle is embedded in more than half is preferred for the amount of embedding, and not ****ing is important for it at the time of the silicon dissolution.

[0041]Next, the crystalline layer of the silica glass mentioned above concerning the invention of the 3rd and the 4th of this invention is described.

[0042]Silica glass metamorphoses into a cristobalite phase in the crystal growth process of the silica glass in the temperature region from which a silicon single crystal is pulled up. Then, if a crystalline layer is made to form in a quartz glass surface beforehand by heat-treating the silica glass crucible which provided a nucleation starting point which was mentioned above to the inner surface in a phase transformation temperature region, the crystal phase of the silica glass formed can be made thicker.

[0043]For example, by heat-treating what was formed in the inner surface of a silica glass crucible rather than the melting point of silicon which was mentioned above by making into a nucleation starting point the enveloping layer of the substance which is a high-melting point in a phase transformation temperature region, The silica glass crucible concerning the invention of the 3rd of this invention which has an enveloping layer of said high-melting point substance in the outermost surface of the crucible inside, and has a crystalline substance silica layer inside this enveloping layer further can be obtained.

[0044]What made the crystalline substance silica particle by which seeding was carried out to the surface field inside a silica glass crucible again, for example as mentioned above the nucleation starting point or by

heat-treating in a phase transformation temperature region, The silica glass crucible concerning the invention of the 4th of this invention which has a crystalline substance silica layer to the surface field of the crucible inside can be obtained.

[0045]When forming a crystalline layer by such a thermal pretreatment, even if the surface roughening process of a silica glass crucible inner surface which was mentioned above is not necessarily indispensable and it only provides crystallization promoting layers (a different crystalline layer from a silica glass presentation, etc.), can do a desired operation effect so, but. The further outstanding operation effect is obtained by combining a surface roughening process further.

[0046]As a manufacturing method of the silica glass crucible which has a crystalline layer of silica glass to the inner surface part of a crucible concerning these 3rd and 4th inventions, it is not limited to the thing in particular illustrated above.

[0047]The thickness of the crystalline layer of the silica glass beforehand formed as mentioned above about the invention of the 3rd and the 4th of this invention, Although what is necessary is just to set up suitably not according to the thing limited especially but according to the time which silicon crystal pulling takes, since it may have an adverse effect on the various characteristics required of the silica glass crucible itself when the thickness of this crystalline layer exceeds 5 mm, as a crystalline layer, a thickness of 5 mm is enough. As for the thickness of a crystalline layer, since the crystal layer of a quartz glass surface does not break or exfoliate in a beta-alpha transformation as occasion demands in cooling a crystallized silica glass crucible to a room temperature, it is preferred that it is 1 mm or less. Although the value of 20 micrometers can be mentioned, for example from a viewpoint that the prominent effect by forming a crystalline layer beforehand in this way is expectable as a lower limit of the thickness of a crystalline layer on the other hand, it may not necessarily be limited to this and may be the thickness not more than this.

[0048]If silica glass is the conditions which cause a phase transformation as heat treatment which forms a crystalline layer, the temperature of heat treatment, time, and atmosphere will not be restricted. However, it is desirable as processing practical and effective from a viewpoint of industrial production nature that it is below not less than 1200 ** of glass-transition temperature and the softening temperature temperature of silica glass as heat treatment temperature. Below 1200 **, the crystallization rate of silica glass is very slow, and obtaining required crystal layer thickness takes time, and it is uneconomical, and is the softening temperature temperature (it is dependent on the quality of a quartz glass material.) of silica glass. Since heat modification of a crucible occurs and it becomes impossible to perform silicon crystal pulling at an elevated temperature from 1650 ** typically, it is not desirable. Since the growth rate of a crystalline layer serves as the maximum at 1600-1700 **, it is desirable to carry out temperature up to this temperature, but it should be cautious of the softening temperature temperature of the silica glass to be used serving as a maximum. What is necessary is just to set up the retention time of heat treatment according to the thickness of a crystalline layer to obtain. The atmosphere in particular that heat-treats is not limited and can form a crystalline layer similarly in steam content atmosphere among an inert gas atmosphere or the atmosphere. This heat treatment may be performed within a crystal-pulling furnace, and it may carry out in another general-purpose heat treating furnace. When carrying out in another heat treating furnace, it becomes possible to make an oxygen density and water vapor pressure high, and the higher rate of crystal growth can be obtained as compared with reducing atmosphere like [in a crystal-pulling furnace]. When

carrying out in another heat treating furnace, the occupation time of a crystal-pulling device may be able to be reduced and it may be advantageous on productivity.

[0049]The silica glass crucible in particular used as a base material in this invention does not limit, what used living rock English powder as the raw material cannot care about it with what used synthetic quartz powder as the raw material, but what is sold as an object for silicon crystal pulling can also be used for it. The size of a silica glass crucible, shape, and the manufacturer in particular do not limit, either.

[0050]

[Example]Below, the example and comparative example of this invention are shown based on Table 1 and Table 2. Each used silica glass crucible was a crucible of marketing manufactured from living rock English powder, and the surface roughness of the caliber of about 455 mm (18 inches) and a crucible inner surface was a thing of the range of 0.003–0.007micromRa.

[0051]The surface roughening process of the silica glass crucible inside all surface was carried out with the diamond belt sander. All had also satisfied the conditions of $R_{max}/R_{min} \leq 10$. Spreading on the silica glass crucible inside all surface of TiO_2 and $CaAl_2O_4$, These powder reagent was mixed with the tetraethoxysilane, it was considered as suspension, and this suspension was applied, it held for 30 minutes, 120 ** was calcinated at 600 more ** for 1 hour, and the crystalline layer of the outermost layer was formed.

[0052]Coat formation on the silica glass crucible inside all surface of TiN and TiC was carried out by the ion plating method. Each enveloping layer was a crystal phase and the ranges of each crystal grain were 0.005 micrometer – 1 micrometer.

[0053]Seeding to the silica glass crucible inside all surface of a silica particle was performed in the following procedures. Cristobalite particles ground the above-mentioned silica glass crucible to 100 micrometers or less, put it into the high-purity-alumina crucible, and were calcinated 1400 ** in argon atmosphere for 5 hours, and what ground this was used for them. In the analysis by the X-ray diffraction method of this powder, it checked that it was cristobalite. The reagent made from High grade Chemicals was used for a quartz watch and silica glass. The sol gel process carried out specified quantity addition churning of water 240 weight section, methanol 53 weight section, and the silica particle, and applied them to the silica glass crucible inner surface at tetramethyl orthosilicate 253 weight section. It dried at the room temperature for about 10 minutes after spreading, and held at 120 ** for 30 minutes. Furthermore, 600 ** of things calcinated for 60 minutes were used with the heating furnace.

[0054]When carrying out preheating of the silica glass crucible which performed each pretreatment and making a cristobalite layer form, it calcinated for 10 hours. When carrying out preheating with a common heating furnace, it heated in the atmosphere and the cristobalite layer was made to form with the piece of silica glass (sample of the size of about $30 \times 30 \times 10 - mm^3$ started from the same kind of silica glass crucible) which performed same pretreatment. It cooled to the room temperature after preheating, and cristobalite layer thickness formed in the sample surface was surveyed by section observation, and this thickness was dealt with for being the same as the cristobalite layer thickness formed in the silica glass crucible inner surface. As a result of carrying out a thin film X diffraction, it checked that any sample was a cristobalite phase as a crystal phase. On the other hand, in carrying out preheating within a raising furnace, similarly it calcinates a crucible for 10 hours in an argon gas style (both the concentration of a steam and oxygen is 100 ppb or less), Crystal pulling was performed succeedingly, the section of the silica glass crucible inner

surface was observed at the room temperature after completion, and it was only presupposed that it is to survey cristobalite layer thickness of a part which did not touch silicon melt.

[0055] Fill up these silica glass crucibles with polycrystalline silicon, it was made to dissolve in them, and a silicon single crystal ingot 150 mm in diameter was manufactured under argon atmosphere by the CZ process. Each examples of raising of all were operated on the same conditions. Manufacture of the always stable silicon single crystal of a crucible was completed without carrying out heat modification. Although it did not rub in the case of which [of an example and a comparative example] but the body part pulled up the ingot which is 500 mm first, except for the comparative example 3, all were able to be pulled up by no transposing. Crystal pulling of the 2nd henceforth is performed after the 1st crystal pulling using the remaining silicon melt. After checking whether it had transposed if the body part raised the ingot which is 500 mm, the ingot pulled up was immersed into silicon melt, and it dissolved altogether, and it repeated until it formed into the owner rearrangement the "raising-remelting" cycle of raising a crystal again. However, untransposed raising in this cycle judged that a maximum of 4 times was enough, and made it end as evaluation of the probability of not transposing here. When an owner rearrangement was formed in the middle of raising, after pulling up to the last, it cooled to the room temperature. The merits and demerits of the crucible life were judged with the number of times which was able to pull up the monocrystal ingot by no transposing, and body length. When an owner rearrangement is formed in a position with a body length [in the middle of the 2nd raising] of 315 mm, under [all / 1.6 / (315/500: 1+ the second place of a a small number of point omission) / number of times / of untransposed raising].

[0056] After pulling up a silicon single crystal, the covering area rate and thickness of the cristobalite layer of the silica glass crucible inner surface were surveyed. In [when the slice wafer of 2 mm thickness cut down from the center of a body part of the untransposed monocrystal ingot pulled up to the 1st time in each example of raising was measured by the infrared absorption spectrum (FT-IR)] all the examples and comparative examples, The oxygen density was within the limits of a $8.5**0.5 \times 10^{17}$ individual / cm^3 (JEIDA standard), and carbon concentration was below a 1.5×10^{15} individual / cm^3 (JEIDA standard).

[0057] Crystal pulling was performed using the usual silica glass crucible as usual which has performed neither of a thermal pretreatment of the processings, comparative example 1 surface roughening process nor promotion of crystallization. When time passed, the owner rearrangement was formed and it became impossible to pull up with a single crystal to the inside of a short time at the beginning of training, although it was possible to have pulled up a silicon single crystal, without forming an owner rearrangement. When the crucible was observed after crystal pulling, while the crucible internal surface was ruined, the cristobalite phase was distributed unevenly. The cristobalite layer coverage on the surface of a crucible was 5%. The conventional crucible shows that a crucible life is [which a tea film and a rough surface occur and has little number of times of untransposed raising of a monocrystal ingot as 1.5] short.

[0058] Although the surface roughening process was carried out to the 2 copies of comparative example Tsuneishi English glass crucible, since surface roughness was as small as 0.01 micrometer, there was almost no crystallization facilitatory effect, and the state on the surface of a crucible was usually as practically equal as the crucible. Therefore, the number of times of untransposed raising is considered to have been equivalent to 1.5 and the conventional crucible. This shows that the surface roughening process of moderate relative roughness is required for promotion of crystallization.

[0059]The surface roughening process of the 1 copy of example Tsuneishi English glass crucible was carried out, and the TiN crystallization promoting layer was formed further. This TiN crystallization promoting layer assumed gold, and it had metallic luster like a mirror plane, and had adhered to the crucible surface, and even if it threw in the polycrystalline silicon raw material, a layer did not exfoliate. Crystal pulling was performed using this crucible. Although the cristobalite layer in contact with silicon melt carried out the erosion selectively with the passage of time, cristobalite layer coverage still maintained 70% far high usually (comparative example 1), and the number of times of untransposed raising has improved to 2.2. This shows that a surface roughening process and crystallization promoting layer formation are effective for glass crystallization.

[0060]After carrying out a surface roughening process to a 2 copies of examples Tsuneishi English glass crucible, the cristobalite particle crystallization promoting layer was formed. Cristobalite particles were stuck to the crucible internal surface, even if it carried out the feeler of them, they did not exfoliate, and even if it threw in the polycrystalline silicon raw material, a layer did not exfoliate. Crystal pulling was performed using this crucible. Cristobalite layer coverage had ** higher than usual in which the cristobalite layer in contact with silicon melt carried out the erosion selectively with the passage of time, and the number of times of untransposed raising has improved to 2.0. This shows that a surface roughening process and the silica particle stratification are effective for glass crystallization.

[0061]After having formed the TiC crystallization promoting layer in the 3 copies of examples Tsuneishi English glass crucible, carrying out preheating within the common furnace for 1500 ** 10 hours and making a cristobalite layer form, it cooled to the room temperature. This crucible was put in in the raising furnace and crystal pulling was performed. The cristobalite layer coverage in a crucible inner surface is as high as not less than 95%, and it means that the cristobalite layer was formed uniformly. For this reason, since exfoliation of the kudzu fragment from the crucible surface was controlled, the number of times of untransposed raising has improved to 3.6. This shows that crystallization promoting layer formation and high temperature firing are effective for glass crystallization.

[0062]After having formed the TiO_2 crystallization promoting layer after carrying out a surface roughening process to a 4 copies of examples Tsuneishi English glass crucible, carrying out preheating within the common furnace for 1500 ** 10 hours and making a cristobalite layer form, it cooled to the room temperature. A crucible internal surface is whitened completely, the precise and uniform cristobalite layer is formed thickly, and the conspicuous crack in particular was not seen. This crucible was put in in the raising furnace and crystal pulling was performed. The cristobalite layer coverage in a crucible inner surface is as high as not less than 98%, and it means that the cristobalite layer was formed uniformly. By this example 4 which added the surface roughening process further to Example 3, since coverage improved since the cristobalite layer became still thicker, and exfoliation of the kudzu fragment from the crucible surface was controlled, it is thought that the number of times of untransposed raising has improved to 5.0.

[0063]Although the surface roughening process of the 3 copies of comparative example Tsuneishi English glass crucible was carried out and the TiO_2 crystallization promoting layer was formed further, since the thickness was thin, promotion of crystallization is considered that were not enough and the cristobalite layer was thin. It is thought that cristobalite layer coverage became halfway 20% since the cristobalite layer in contact with silicon melt carried out the erosion selectively with the passage of time, the rough surface of

the crucible advanced and the number of times of untransposed raising became 1.3, the conventional crucible, and below equivalent. This shows that moderate crystallization promoting layer thickness is required for promotion of crystallization.

[0064]Although the surface roughening process of the 4 copies of comparative example Tsuneishi English glass crucible was carried out and the CaAl_2O_4 crystallization promoting layer was formed further, The thickness was too thick, the preheating treatment of 1540 ** 10 hours became too effective with the general-purpose heating furnace further, the promotion of crystallization became high exorbitantly at the sake, and the cristobalite layer became thick with about 2 mm. When it once cooled to a room temperature, the crack arose in the cristobalite layer. The cristobalite layer in contact with silicon melt exfoliates selectively in crystal pulling, and the inside of melt is floated, it adheres to a silicon single crystal interface, and it is thought that the number of times of untransposed raising fell in 0.7. Thus, since the crucible could be calcinated comparatively uniformly in a general-purpose heating furnace and it calcinated in atmosphere where an oxygen density and water vapor pressure are high, promotion of crystallization was able to be made very high. Although the preheating temperature of 1540 ** is high when supplemented just to make sure, there is also an advantage that preheating time can be shortened. Since the cristobalite layer became thick with about 2 mm far over 1 mm here, the crack arose in the cristobalite layer, but if preheating time is shortened, controlling a cristobalite layer to 1 mm or less will also add the possible thing.

[0065]Formed the Quartz particle crystallization promoting layer in the 5 copies of examples Tsuneishi English glass crucible, and put in in the raising furnace, carried out preheating for 1380 ** 10 hours, the cristobalite layer was made to form in sufficient thickness, and crystal pulling was performed succeedingly. Cristobalite layer coverage is as high as not less than 80%, and it means that the cristobalite layer was formed uniformly. Therefore, it is thought that the number of times of untransposed raising has improved to 2.4.

[0066]After carrying out a surface roughening process to a 6 copies of examples Tsuneishi English glass crucible, formed the Quartz particle crystallization promoting layer, and carried out preheating within the raising furnace for 1380 ** 10 hours, the cristobalite layer was made to form, and crystal pulling was performed succeedingly. Cristobalite layer coverage is as high as not less than 90%, and it means that the cristobalite layer was formed uniformly. Therefore, it is thought that the number of times of untransposed raising has improved to 2.7. It turns out that the number of times of untransposed raising is improved more for this example 6 with which the surface roughening process is compounded as compared with Example 5. It turns out that the number of times of untransposed raising is improved more for the technique of this example 6 in which high temperature firing is compounded as compared with Example 2.

[0067]After carrying out a surface roughening process to a 7 copies of examples Tsuneishi English glass crucible, formed the silica glass particle crystallization promoting layer, and carried out preheating within the raising furnace for 1380 ** 10 hours, the cristobalite layer was made to form, and crystal pulling was performed succeedingly. Since the particle diameter of silica glass particles was made detailed with 4 micrometers, and the volume rate was made high with 90% and seeding of many fine crystal cores was carried out, cristobalite layer coverage will be as high as not less than 95%, and a cristobalite layer will be formed uniformly. Therefore, it is thought that the number of times of untransposed raising has improved to 3.9.

[0068]

[Table 1]

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6
石英ガラス表面粗度 R a (μm)	0.1	0.9	<0.01 (無処理)	1.8	<0.01 (無処理)	5.4
結晶化促進剤種類	TiN	クリストバライト	TiC	TiO ₂	クォーツ	クォーツ
結晶化促進剤平均粒径 (μm)	0.01	60	0.04	0.1	110	110
結晶化促進剤体積率 (%)	100	75	100	100	25	25
結晶化促進層厚み/深さ (μm)	2	10	0.1	0.05	20	20
予備熱処理	—	—	一般炉	一般炉	引上炉	引上炉
予備熱処理温度 (℃)	—	—	1470	1470	1380	1380
予備熱処理後クリストバライト層厚さ (μm)	—	—	60	860	—	—
引上後クリストバライト層被覆率 (%)	70	60	>95	>98	80	90
引上後クリストバライト層厚さ (μm)	50	20	20	210	20	20
無転位 引上回数	2.2	2.0	3.6	5.0 (引上打切)	2.4	2.7

[0069]

[Table 2]

	実施例 7	比較例 1	比較例 2	比較例 3	比較例 4
石英ガラス表面粗度 R a (μm)	17.5	<0.01 (無処理)	0.01	5.4	17.5
結晶化促進剤種類	シリカガラス	—	—	TiO ₂	CaAl ₂ O ₄
結晶化促進剤平均粒径 (μm)	4	—	—	0.1	0.01
結晶化促進剤体積率 (%)	90	—	—	100	100
結晶化促進層厚み/深さ (μm)	10	—	—	0.005	60
予備熱処理	引上炉	—	—	一般炉	一般炉
予備熱処理温度 (℃)	1380	—	—	1500	1540
予備熱処理後クリストバライト層厚さ (μm)	—	—	—	10	2130
引上後クリストバライト層被覆率 (%)	>95	5	5	20	30
引上後クリストバライト層厚さ (μm)	30	5	5	5	1890
無転位 引上回数	3.9	1.5	1.5	1.3	0.7

[0070]

[Effect of the Invention] In this invention, a uniform crystal phase can be extensively formed in a silica glass

inner surface, and only thickness required not only for a crucible inner surface but a thickness direction can be crystallized.

Therefore, exfoliation of the piece of silica kudzu from the crucible surface which was a problem conventionally can be controlled dramatically, and the silica glass crucible for silicon crystal pulling which is equal to prolonged use rather than the conventional silica glass crucible as a result can be provided. This became possible to pull up a silicon single crystal with the sufficient yield for a long time, and the industrially advantageous effect that a silicon single crystal could be manufactured at substantially low cost compared with the former was revealed.

[Translation done.]